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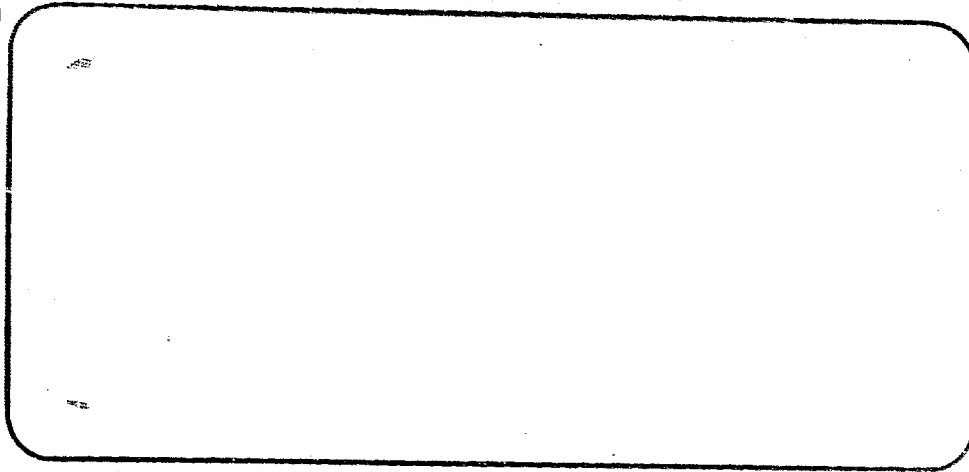
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"RESEARCH ON TRIPLET STATES
AND PHOTOCHROMISM"

ANNUAL REPORT 1963

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FOREWORD

This report was prepared by the Physical Research Division of Space Technology Laboratories, Inc. under USAF Contract No. AF-41(609)-1457. This contract was initiated under Project No. 7753 and Task No. 27612 by Major. A. V. Alder of the School of Aerospace Medicine, Aerospace Medical Division, with Maj. John Colianna as the contracting officer. The contract is administered by Ballistic Systems Division (AFSC), AF Unit Post Office, Los Angeles 45, California.

Research under this contract is being carried out in the Quantum Chemistry Department of the Quantum Physics Laboratory under the supervision of Dr. Maurice W. Windsor. The following persons have contributed to the research studies and to the preparation of this report:

Dr. M. W. Windsor	Department Head and Project Manager
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Dr. W. R. Dawson	Member of the Technical Staff
Dr. J. R. Kropp	Member of the Technical Staff
Mr. R. S. Moore	Member of the Technical Staff

Technical support has been provided by Mr. C. Krull, Mr. C. C. Stanley, by the STL Glass Shop and by the Research Division Model Shop. Secretarial assistance was rendered by Miss Ethel Dunn.

This report covers work carried out between 1 January, 1963 and 24 January 1964.

ABSTRACT

This report describes research studies on the photochromic properties of the triplet states of aromatic compounds and their application to the problem of eye-protection against nuclear weapons.

A Cary spectrophotometer has been specially modified to allow the transmission of a sample to be measured while it is under irradiation by a repetitively triggered flash lamp. Using this apparatus, triplet-triplet absorption spectra have been recorded for several new compounds in plastic media. Coronene, naphthocoronene and naphthochrysene are all found to have strong T-T absorption extending over most of the visible region.

Several methods have been tried for measuring T-T extinction coefficients. The main obstacle is overlap of the long wavelength singlet absorption by T-T absorption, thus preventing measurements of singlet depletion. This problem has been circumvented by making depletion measurements at shorter wavelengths, using an organic solvent frozen to a glass at 77°K, together with a flash method of excitation. Naphthocoronene appears to have an ϵ exceeding 10^5 .

Quantum yields of fluorescence have been measured and used to estimate the efficiency of triplet formation. Using certain reasonable assumptions, triplet yields of 70% or better are estimated for most of the compounds studied.

Improved plastics have been found in which much higher concentrations of aromatic compounds can be dissolved, thus permitting the use of thinner specimens.

Fatigue studies show no detectable fatigue after 700 flashes for chrysene in polymethylmethacrylate.

The possibility of using a photochromic filter with its own built-in source of excitation is discussed. Excitation by U-V light is favored over excitation by electron irradiation. A flash lamp of about 1000 Joules capacity is required, using naphthocoronene, the best triplet compound available to date. For this energy, the flash lamp and its associated power supplies would weigh about 100 lbs.

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I. Introduction

A. Flash Blindness and Retinal Damage

Exposure of the eye to high intensity flashes of light, such as those from a nuclear explosion, can cause flash blindness and even permanent damage to the retina. The human blink time of about 0.1 sec is not short enough to protect the eye against damage from the flash of a nuclear weapon. The most desirable solution to this problem would be to prevent bursts of high intensity light from reaching the eye, by means of a rapidly responding automatic light filter which is normally transparent, but which becomes opaque or highly absorbing when the light intensity suddenly increases. Although electromechanical goggles have been designed to accomplish this task, photochromic devices offer far greater simplicity and reliability and would readily lend themselves to a much wider range of applications. As demonstrated in previous reports, aromatic hydrocarbons and their derivatives, dissolved in a suitable plastic medium, exhibit strong, reversible, photochromic effects on irradiation because of temporary excitation to the lowest triplet state. Automatic light filters using triplet states appear to offer attractive possibilities for flash blindness protection.

B. Requirements for an Ideal Photochromic Filter

The following specifications have been provided by the Air Force for an ideal automatic light filter to protect personnel against flash blindness and retinal damage:

1. Reach optical density of 4 (99.99% absorption) over the whole visible spectrum within 500 microseconds.
2. Recover normal transparency in less than 2 seconds.
3. Approximate a neutral filter for the visible region.
4. Have a 75% or better transmission in the inactivated state in sunlight.

5. Be capable of repeated exposures without fatigue.
6. Have good optical quality.

Satisfaction of all the above requirements would lead to an ideal system. Even a partial ability to meet these criteria would constitute a beneficial improvement in the present state of the art.

C. Evaluation of a Triplet State Filter

An analysis of the problem of protection against flash blindness and a detailed evaluation of triplet state automatic light filters has been given in the Annual Report for 1962. The major points are summarized here to provide continuity of discussion.

Many aromatic hydrocarbons normally absorb only in the ultra-violet and are therefore colorless. Exposure to intense U-V light, however, temporarily and instantaneously converts many of the molecules to the lowest triplet state. If, as often happens, the triplet molecule absorbs visible light, the result is a change in color. Triplet molecules are metastable and, in the absence of further strong excitation, rapidly return to the original ground state. Thus the change in color is reversible. The time for this reversal depends on the medium surrounding the triplet molecule. In fluid solvents it is about 10^{-4} sec, whereas in rigid plastic media it is of the order of 1 sec. The process of excitation, on the other hand, is not dependent on the medium and takes place instantaneously even in rigid plastics. It is therefore possible to make automatic light filters for practical evaluation, by incorporating a suitable aromatic compound into a plastic medium of good optical quality.

The speed with which such a filter darkens depends on the rate of arrival of the U-V energy which activates it. The best method of evaluation is to ask the following questions,

1. How much U-V energy in cal/cm² is needed for the filter to reach an optical density of, say, 1 throughout the visible region?
2. Of the visible radiation which accompanies the U-V energy, how much is transmitted by the shutter as it progressively darkens?
3. Is the total amount of visible energy thus transmitted likely to be dangerous?

This was done in the 1962 Annual Report and the following simple expression obtained for the unit of U-V energy, E, (for an average excitation wavelength of 3650A), which must be absorbed to produce an optical density equal to one in the visible,

$$E = \frac{73}{\epsilon \phi} \text{ cal/cm}^2 \quad (1) *$$

To reach an optical density of 2, twice this amount is required. Similarly an optical density of 4 requires an amount of U-V energy equal to 4E. However, because the triplet filter darkens in an exponential fashion, only 40% of the visible light which accompanies the first E unit of U-V is transmitted, only 4% for the second E unit, and so on. Thus the total amount of visible light which gets through the triplet shutter while it is in the process of closing is only 44.44 % of the visible light unit which accompanies one E unit of U-V energy.

Let us denote this accompanying unit of visible light by V. The relative sizes of V and E will depend on the spectral distribution of the source, which in turn depends on its temperature. Also, whereas for retinal damage considerations, the whole visible range between 4000 and 7000A must be used in calculating V, for flash blindness calculations, a narrower range which takes account

* ϵ = molar decadic extinction coefficient for T-T absorption

ϕ = quantum yield of triplet formation.

of the varying spectral response of the retina, can be used. For example, for red or blue light at the tails of the eye's sensitivity curve, much higher light intensities would be needed to induce flash blindness than for light whose wavelength matches the eye's peak sensitivity at 5500A.

Flash blindness can occur at light levels well below the threshold for retinal burns and is therefore harder to protect against. For a black body source at 7600°K, the relationship between V and E, taking into account only radiation between 5000 and 6000 A in calculating V, and radiation between 3200 and 4000 A for E is, given by,

$$V = \frac{13}{14} E \quad (2)$$

However, only 44.44% of this (denoted V_t) is actually transmitted.

Thus, $V_t = 0.4 E$ (3)

From the data of Metcalf and Horn (1), we find that the maximum exposure for which the recovery time (for a test stimulus of 7 ft. lamberts luminance) was immediate, was 3200 lumens/ft² for a 0.1 sec exposure. This exposure is equivalent to 1.33×10^{-4} cal/cm² of visible energy. Thus we require that V_t be equal or less than this figure,

$$V_t = 0.4E \leq 1.33 \times 10^{-4} \text{ cal/cm}^2 \quad (4)$$

Substituting for E from equation (1) we get,

$$0.4 (73/\xi) \leq 1.33 \times 10^{-4}$$

or $\xi \geq 2.3 \times 10^5$ (5)

The maximum value of ϕ , the quantum efficiency of triplet formation, is unity. Thus the minimum value of ϵ for protection is 2.3×10^5 . Furthermore this value of ϵ must be maintained at least throughout the region of maximum eye sensitivity between 5000 and 6000Å. It is clear that ϵ is perhaps the most important single parameter in evaluating compounds for flash blindness protection.

To summarize then, an optimum compound for flash blindness protection, should have the following properties,

1. Extinction coefficient $\epsilon \geq 2.3 \times 10^5$ (molar decadic units).
2. High quantum yield ϕ of conversion to the triplet state, preferably approaching unity.
3. Broad T-T absorption throughout visible region of the spectrum.
4. Triplet lifetime in the range 0.1 sec to a few seconds. This provides reasonably rapid recovery of transparency without being so short as to reduce the efficiency of the excitation process.
5. Be photochemically stable to repeated exposures.
6. Have good optical quality.

D. Summary of Research Results

1. Triplet-triplet absorption spectra have been recorded for several new compounds in plastic media, using a specially modified Cary spectrophotometer in which the transmission is measured while the sample is being irradiated by a repetitively triggered flash lamp.

2. Attempts to measure T-T extinction coefficients have met with many obstacles, especially the overlap of T-T absorption with the long wavelength singlet absorption. Most of the problems

appear to have been surmounted by doing experiments in a frozen organic glass at 77°K, using a flash excitation technique. Singlet depletion is now readily observable and reliable values of extinction coefficients should be obtained shortly.

3. Quantum yields of fluorescence have been measured for a series of compounds and used to estimate the efficiency of triplet formation. The majority of compounds studied appear to have triplet yields of 70% or better.

4. Improved plastics have been found in which much higher concentrations of aromatic compounds can be dissolved, thus permitting the use of thinner specimens.

5. Fatigue studies for chrysene in polymethylmethacrylate show no detectable fatigue after 700 flashes.

6. Calculations of U-V irradiation intensities needed to produce an optical density of 4 have been made for several values of ϵ and ϕ .

7. Using the data obtained, compounds have been evaluated for both a passive automatic light filter and for a filter with its own built-in source of excitation. The compound naphthocoronene appears capable of giving good protection against flash blindness if activated by a 1000 Joule flash lamp.

The most important objective for future work is more reliable values of T-T extinction coefficients.

II. Triplet-Triplet Absorption Spectra

A. Apparatus

During the past year T-T absorption spectra of a number of compounds incorporated into polymethylmethacrylate plastic have been measured. The apparatus used was the specially modified Cary spectrophotometer with repetitive flash excitation of the sample. The flash lamp is modulated at the same frequency (60 cps) as the internal beam chopper of the Cary. The relative phase is so adjusted that the lamp flashes only when the instrument is not "looking" at the sample. In this way fluorescence and scattered light from the flash lamp are completely eliminated. A more detailed description of the apparatus has already been given in the last semi-annual report (2).

B. Results

A typical result is given in Figure 1, which shows experimental curves for a plastic sample containing coronene and for a comparison sample of clear plastic containing no solute. Since the instrument must be used on single-beam operation when employing the above technique, the trace for the clear plastic is not simply a horizontal line, representing 100% transmission, as in the double-beam case. Because there is no compensation for the way in which the output of the measuring source and the response of the photomultiplier vary with wavelength, the overall deflection sensitivity changes markedly with wavelength. Beyond about 6500A, the photomultiplier response falls rapidly to zero, while below about 3200A the clear plastic itself begins to absorb.

The curve for the coronene sample without flash excitation closely follows that for the clear plastic, except for the appearance of the singlet absorption bands of the coronene below about 4500A. When the flash excitation is turned on, however, the transmission drops markedly over the whole wavelength region, as shown

in the lowest curve. The difference between the "unirradiated coronene" and "irradiated coronene" curves represents triplet-triplet absorption. It can be readily seen that there is a broad T-T absorption peak at about 4800Å. Hopefully, also, the lower curve should cross and rise above the "unirradiated coronene" curve at some point, indicating depletion of the singlet absorption. Unfortunately, for coronene and several other compounds, the T-T absorption overlaps the normal long-wavelength singlet absorption, making it impossible to observe the singlet depletion in this region and calculate T-T extinction coefficients. We discuss ways of overcoming this problem in Section III.

Spectral curves of optical density versus wavelength for the T-T absorption are obtained by calculating the optical density, $\log \frac{I_0}{I_t}$, at each wavelength, where I_0 and I_t are the relative deflections for the clear plastic and the irradiated coronene sample respectively.

Spectral curves of T-T absorption obtained in this manner are shown in Figures 2,3 and 4 for coronene, naphthocoronene and naphthochrysene. Notice that, for all three of these compounds, the T-T absorption covers most of the visible spectrum and, for naphthochrysene, even extends beyond 7000Å into the near infra-red. By mentally superimposing the three curves, one can see that a mixture of all three compounds should provide a system which maintains a high level of T-T absorption throughout the visible region.

In addition to the above compounds, which have the maximum potential for flash-blindness protection, a number of other compounds such as naphthalene, anthracene, phenanthrene, and chrysene were also studied. T-T absorption spectra for these and other compounds are given in previous reports (2,3). Since the T-T absorption spectra of these compounds have been previously studied (4,5,6), this enables us to compare our results with independent

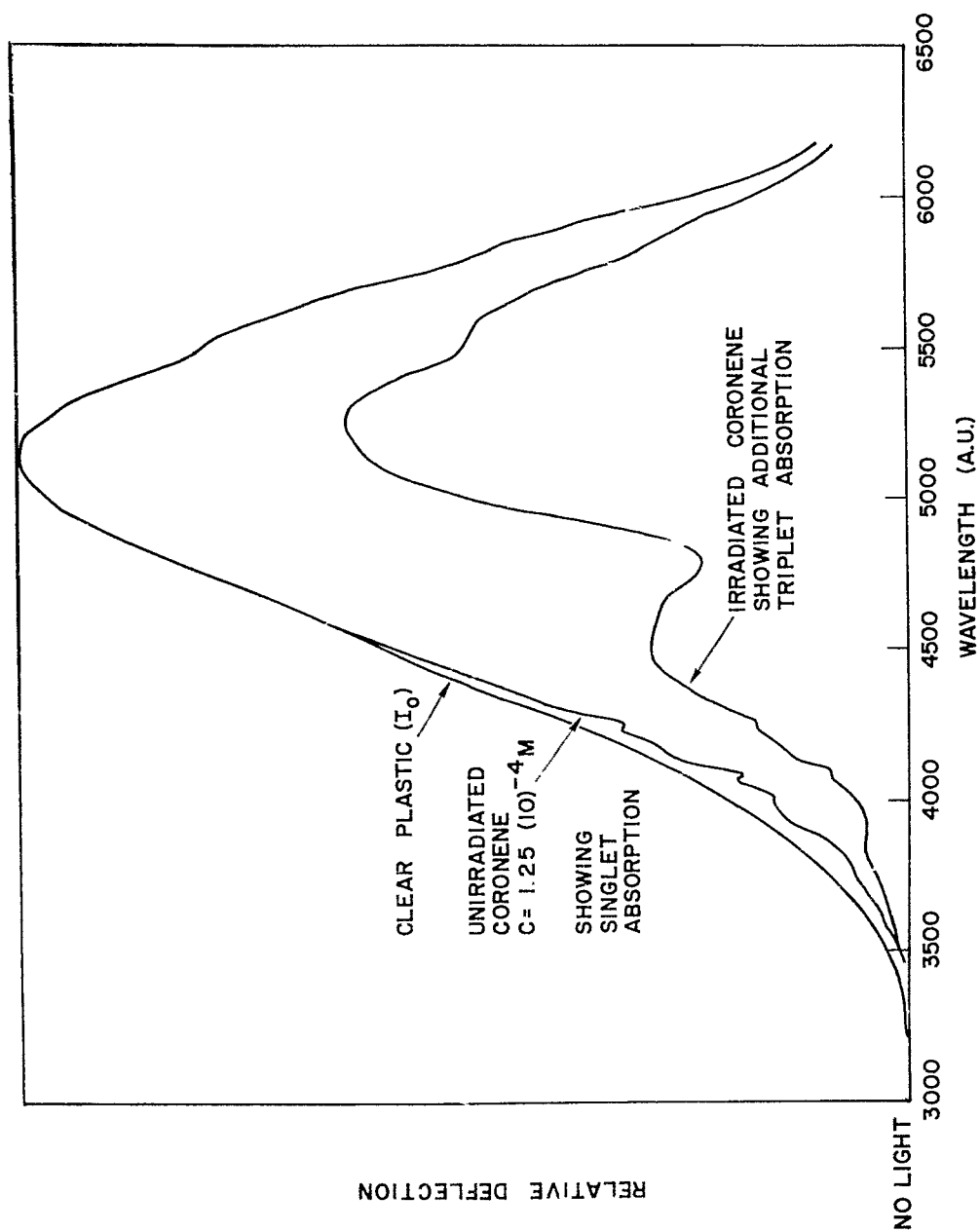


Figure 1. Spectrophotometer Traces for T-T Absorption of Coronene

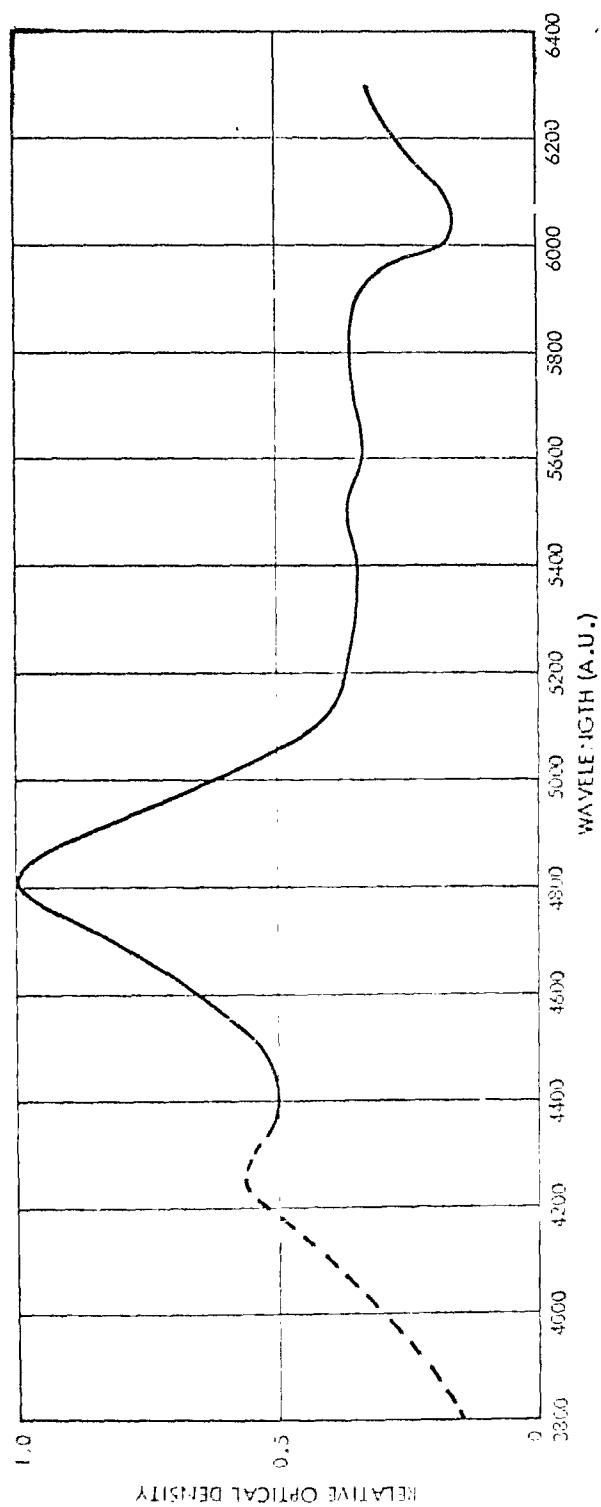


Figure 2. T-T Absorption of Coronene

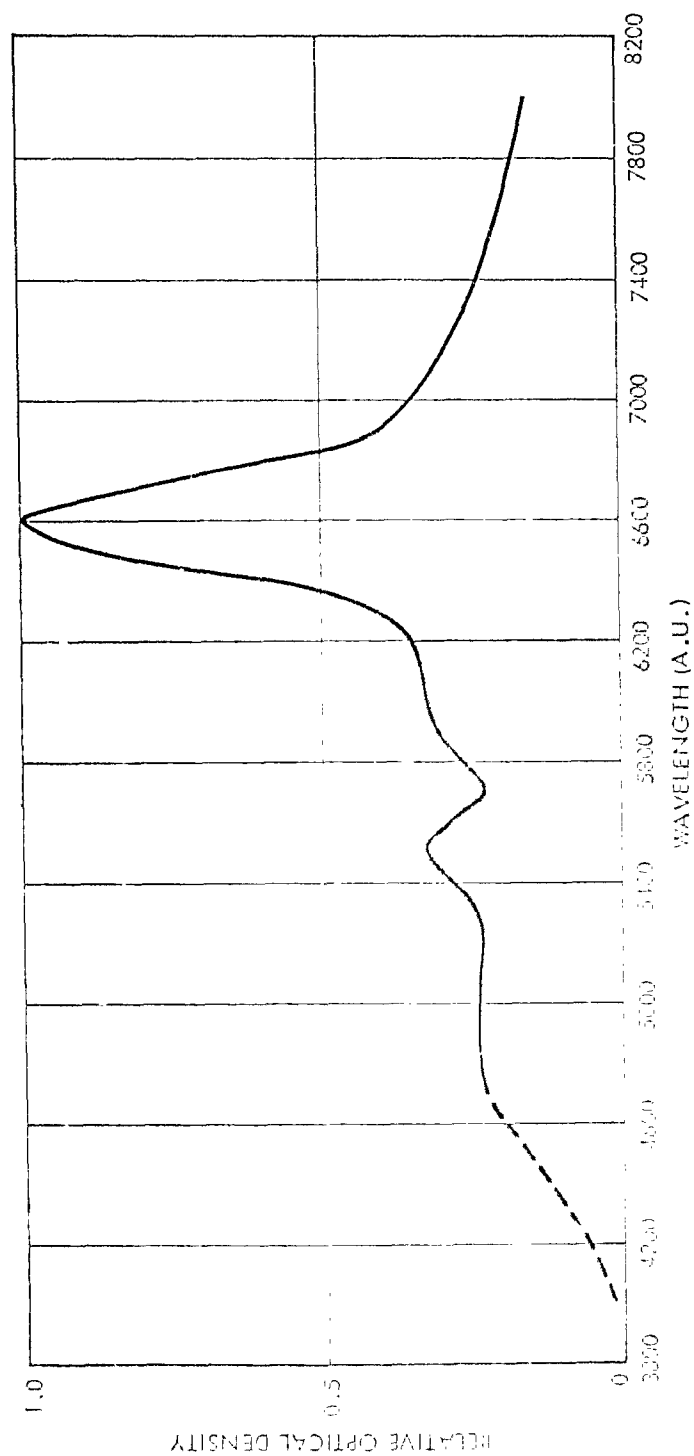


Figure 1: The curve of N465+500nm range

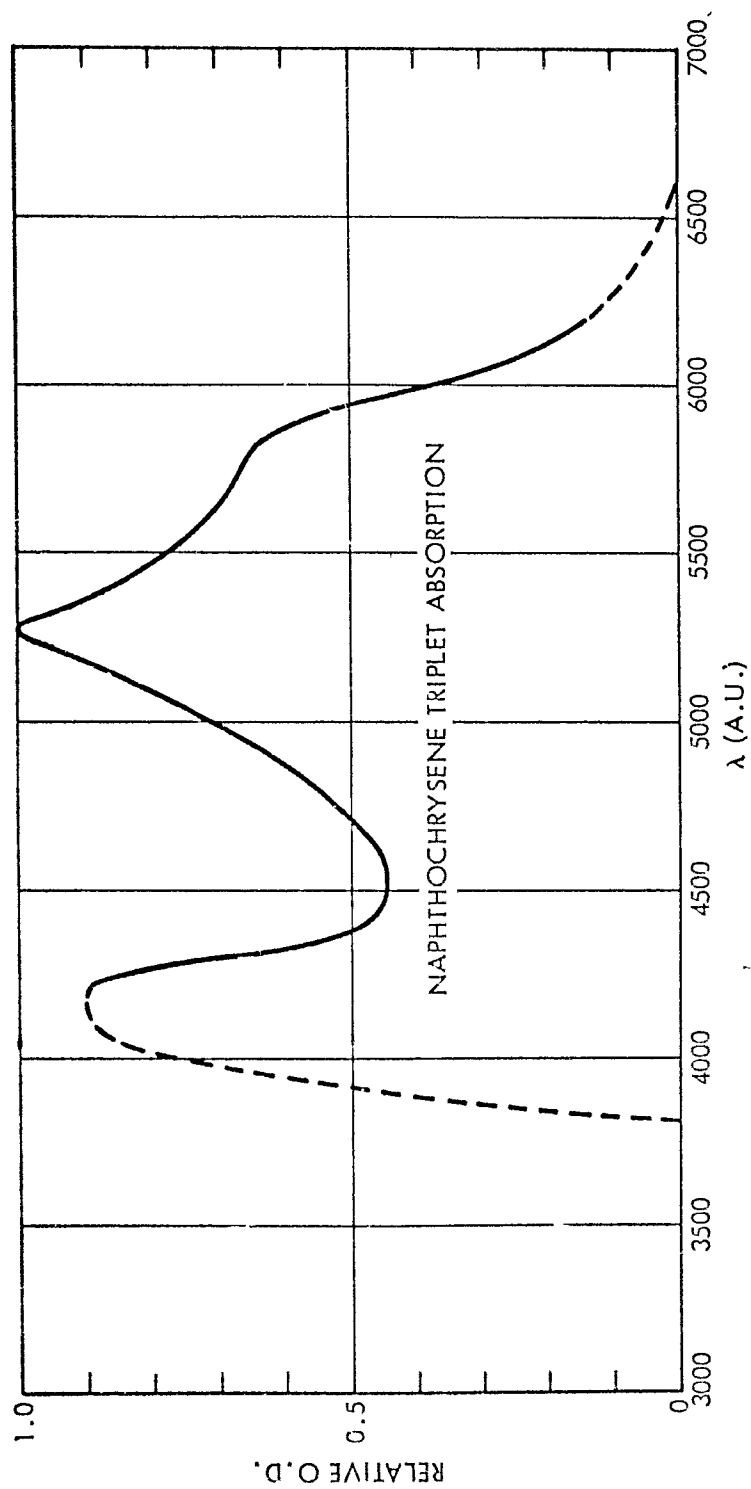


Figure 4. T-T Absorption of Naphthochrysenes

measurements. A good measure of agreement is found for both the wavelengths of peak absorption and the relative intensities of the various bands. Also, these compounds are more favorable for trying to observe singlet depletion, since there is less overlap of the T-T absorption with that of the singlet.

C. Substituted Aromatic Hydrocarbons

Small samples of four quinones of coronene, naphtho-coronene and naphthochrysene were obtained from Dr. Clar. T-T absorption data for these compounds were given in the last semi-annual report (2). Two of the compounds seem promising with regard to the extent of their T-T absorption. It remains to measure their quantum efficiencies and extinction coefficients. To do this larger quantities of each compound are needed. The possibility of custom synthesis by a local chemical company is being investigated. It will be remembered that the possible advantage, offered by O- and N-substituted compounds, is a more efficient conversion to the triplet state.

III. Triplet-Triplet Extinction Coefficients

Considerable effort has been devoted during the past year to attempts to measure the extinction coefficients of T-T transitions. To do this, T-T absorption and the concomitant decrease in singlet absorption must both be measured. Since the extinction coefficient for the singlet is known from the literature (7), or can readily be measured in a separate experiment, it is then possible to calculate how many molecules have been converted from the singlet to the triplet state. Knowing the concentration of triplet molecules, the ordinate scale of the T-T absorption curve can be converted from optical density to extinction coefficient.

Initially our Cary Model 14 spectrophotometer was modified to permit recording the absorption spectrum of a plastic sample while it was being irradiated by the light from a 1000 watt AH-6 mercury lamp. Scattered light from the lamp and fluorescence from the sample made observations of singlet depletion impossible. These problems were solved by using a modulated flash lamp as described in Section II.

Despite these improvements, it was possible to observe a definite singlet depletion for only two compounds, anthracene and coronene. In other cases, singlet depletion was masked by T-T absorption at the same wavelength. For these compounds, estimates of the amount of overlying T-T absorption were made and subtracted from the experimental curves to give an estimated depletion. This leads to a rough estimate for the extinction coefficient. The data are summarized in Table I.

In two cases, naphthochrysene and picene, there was no overlap and still no depletion was seen. By estimating the minimum depletion detectable by our apparatus, we arrive at minimum estimates for the extinction coefficients of these compounds. Where available, data from the literature are also included in the table. For

Table I
Extinction Coefficients of Triplet States of Aromatic Compounds

Compound	Triplet		Literature Values	
	ϵ	λ (A.U.)	(d)	(e)
c Anthracene	30,000 \pm 30%	4240	71,500 \pm 50%	45,000
a Chrysene	\sim 26,400	5800	8,800 \pm 50%	
a Coronene	\sim 100,000	4800	1,000 \pm 50%	
a 1,2,3,4-Dibenz-anthracene	\sim 15,200	4470		
b Naphthochrysene	\geq 43,400	5300		
c Naphthocoronene	151,000 \pm 45%	6600		
a Phenanthrene	\sim 4,800	4860		
b Picene	\geq 11,700	5900		

a. Singlet depletion masked by triplet absorption

b. No singlet depletion observed

c. Singlet depletion observed

d. Porter, G. and M. W. Windsor, Proc. Roy Soc. A., 245
238 (1958)

e. Craig, D. P., and I. G. Ross, J. Chem. Soc. (London),
1589 (1954)

anthracene the values agree within their several limits of error. For coronene there is a large difference in the two values. However, if we make the assumption that all of the coronene (1.08×10^{-4} moles/litre) has been converted to the triplet in our experiments, we obtain a value of 2020 for the extinction coefficient. This is the lowest value possible. The figure of 1000 reported by Porter and Windsor is, therefore, almost certainly too low. These discrepancies cannot be further resolved without more experiments.

The two major problems to be overcome in obtaining improved extinction coefficient data are,

1. Overlap of T-T absorption and singlet absorption
2. Insufficient percentage conversion to the triplet state, resulting in a singlet depletion too small to be measured.

The first problem can in principle be solved by measuring the singlet depletion in a different region of the spectrum. Where overlap between the T-T and the singlet spectra occurs, it usually does so in the long wavelength region of the singlet spectrum, where the singlet absorption is relatively weak. At shorter wavelengths the T-T absorption decreases, while the singlet absorption increases in strength. Thus, the same percentage singlet depletion will lead to a bigger optical density change at shorter wavelengths, while interference from overlap will be reduced. The second problem can be overcome by pumping over a broader wavelength range and by increasing the intensity of the excitation source. With the repetitive flash lamp this could not be done since the lamp was already being operated close to its power limit. In addition, the plastic matrix absorbs strongly below about 3200Å. The above problems can be solved by changing to a different solvent with better ultra-violet transmission and by designing an experiment in which the data can be gathered with a single flash. Much higher peak light intensities can then be used, thus producing larger amounts of singlet depletion.

It appeared that the best way to do this was to dissolve the photochromic compound in a solvent mixture, which could be frozen to

a glass of much greater transmission in the ultraviolet region, thereby permitting more energy to be pumped into the singlet region. The freezing to a glass was necessary for two reasons. In the liquid state the increased photolysis energy (up to 450 joules per flash) produced considerable bubble formation in the solvent, thereby changing the transmission in an arbitrary manner; also, the lifetime of the triplet is too short for convenient measurement of absorption unless the matrix viscosity is increased. A schematic diagram of the experiment is given in Figure 5. The changes in transmission with time after flashing, at both the triplet and singlet wavelengths, are monitored using a mercury lamp source, a beam splitter, two monochromators, photomultiplier detectors and an oscilloscope. Experiments are carried out at liquid nitrogen temperatures and require a special jacketed cell, shown in Figure 6.

Preliminary measurements of chrysene in a frozen glass of 7:1 isopentane-butanol showed a considerable singlet depletion, such as has not been observed previously, and indicate that, good measurements of triplet extinction coefficients should be obtainable for many of the compounds previously studied. Two typical oscilloscope traces are shown in Figures 7 and 8. Figure 7 shows the decay of T-T absorption following the flash, while Figure 8 shows the initial singlet depletion and the subsequent return of the singlet absorption.

The cell used initially had a path length of 5.2cm. This was found to be too short to provide an accurate measurement of singlet depletion. In addition, the source, an Osram 100 watt mercury lamp (HBO-100-W2), caused some depletion by itself. If the transmission in the singlet region is too high, singlet depletion, producing more transparency, provides a very small change in an already large light signal. The collimator apertures and spectrometer slits cannot be reduced much more without running into alignment problems and introducing noise due to minute motions of the source arc image over the slit width. On the other hand, if the source intensity is reduced and the amplifier gain increased, intolerable electronic noise is introduced. Not much increase in absorber concentration can be tolerated because of solubility problems. Therefore, we are forced to go to a longer

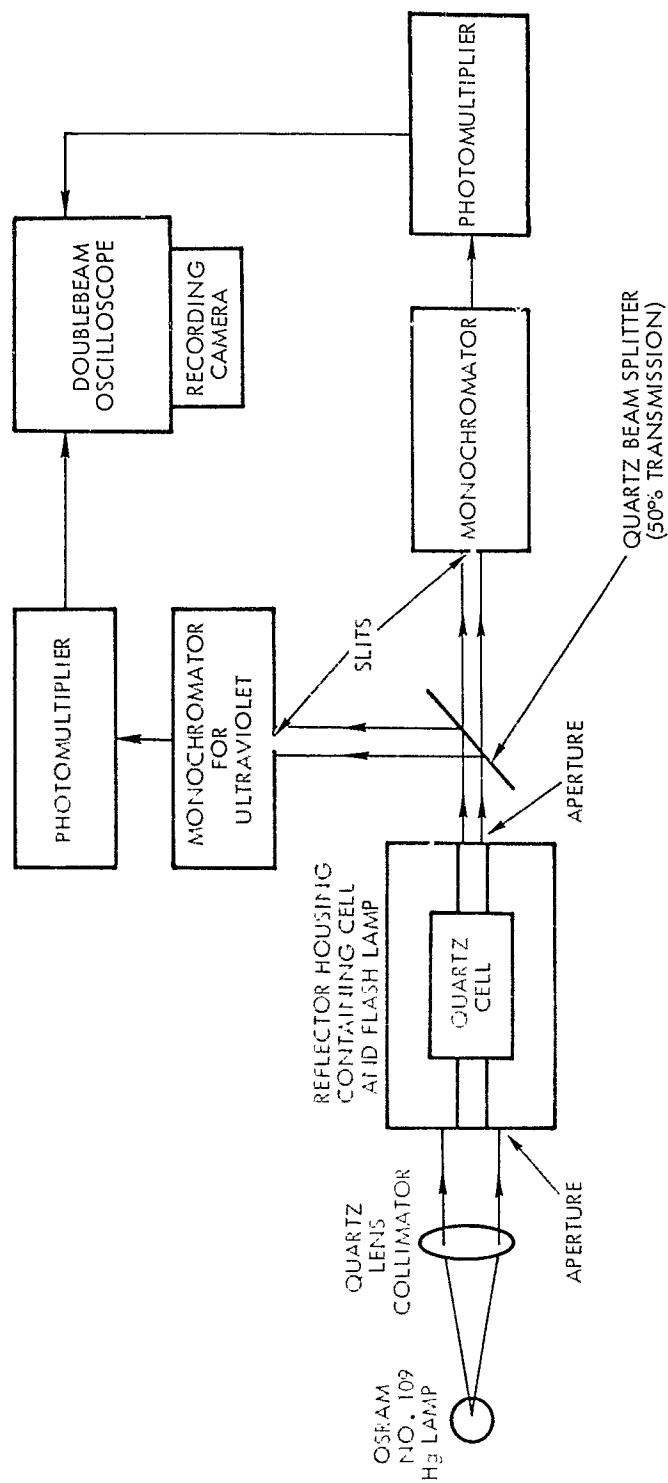


Figure 5. Schematic of Apparatus for Recording Optical Density Changes

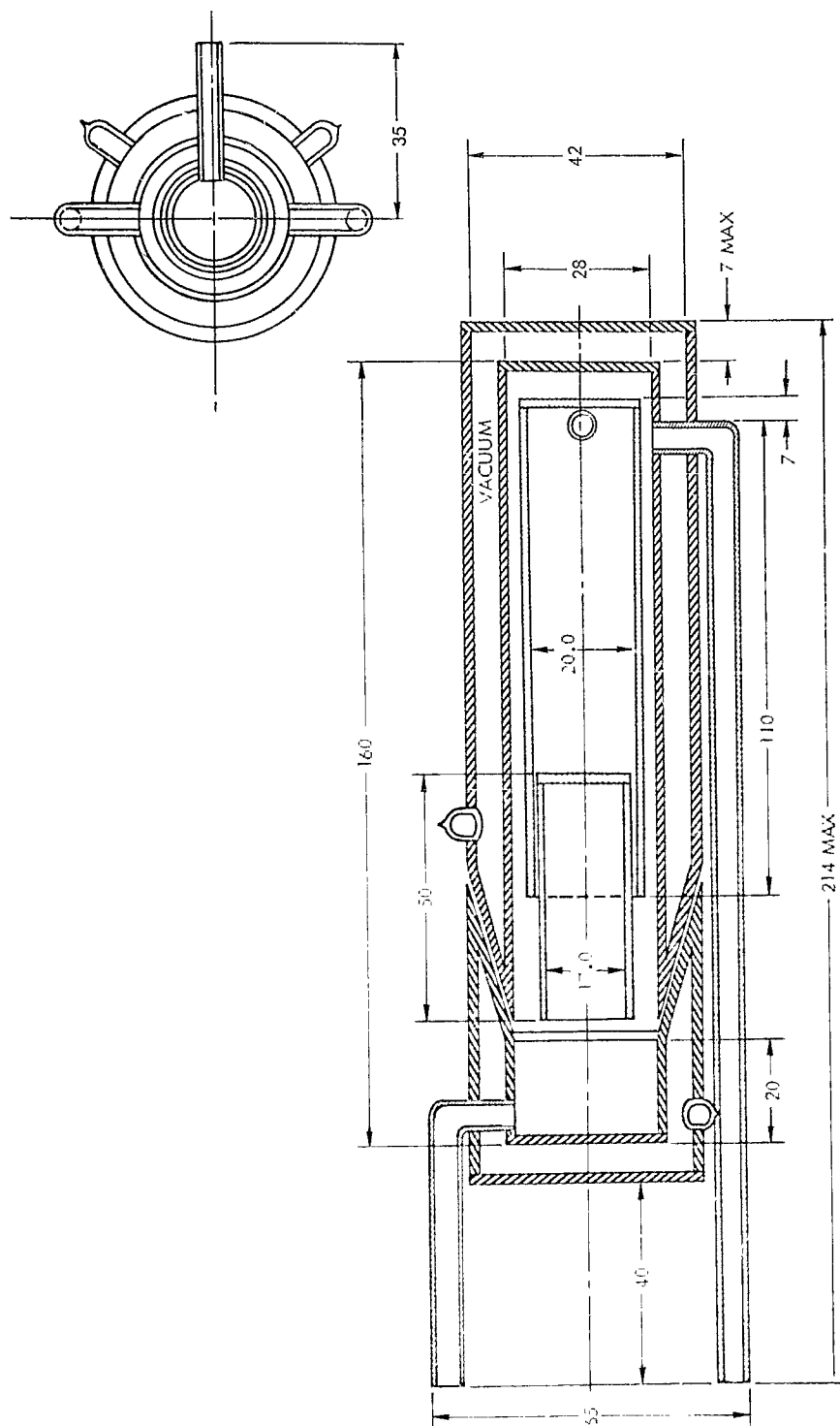


Figure 6. Low Temperature Absorption Cell

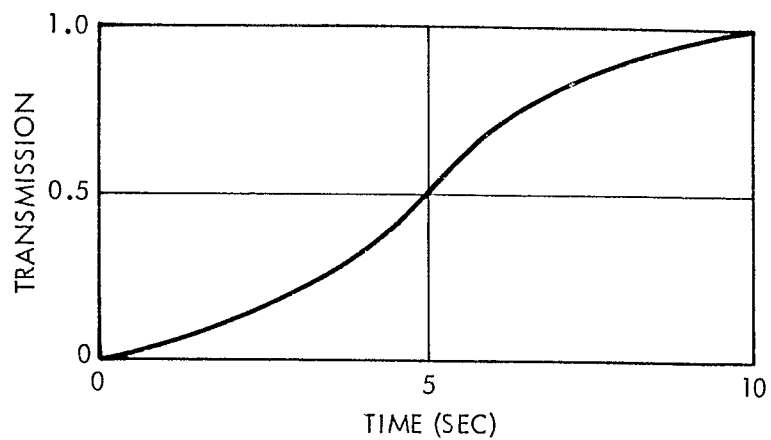


Figure 7. Decay of T-T Absorption after Flashing

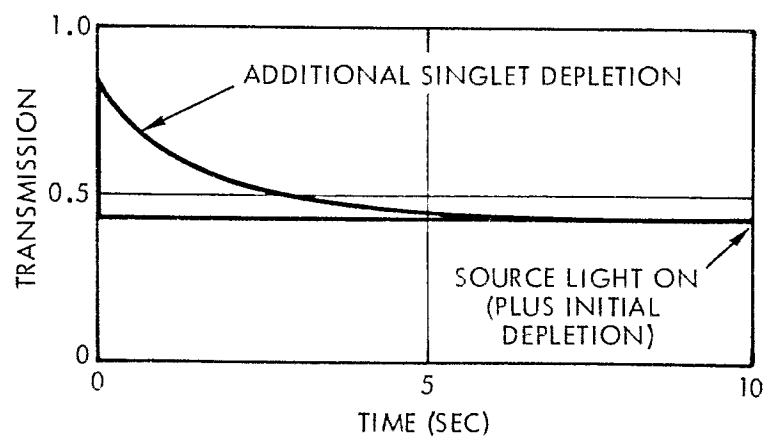


Figure 8. Singlet Depletion on Flashing and Subsequent Return of Singlet absorption

path length, using the present near optimum concentrations and instrument settings, in order that the signal is reduced to a point where singlet depletion produces a large change so that measurement errors are minimized.

Therefore, we are concentrating on accurate measurement of singlet depletion, which has been the most difficult part of the program so far. A new cell with a length of 10 to 15cm has been designed and will be built upon receipt of new quartz tubing. It is expected, judging from the present rough data on chrysene, that it will be possible with this cell to observe singlet depletion for other compounds, except possibly for those whose triplet overlap is so strong that separation is impossible. One interesting fact already observed is that, at least with chrysene, a point in the singlet region has been found where little or no such overlap is present, thus making possible greatly improved accuracy of measurement. This was not observed heretofore, because it occurs at a wavelength opaque to the plastic media used in previous experiments.

Using this new apparatus, the values obtained for chrysene at 5710A are,

$$\epsilon_T \leq 60,000 \text{ using } \epsilon_S = 12,600 \text{ at } 3200A$$

and

$$\epsilon_T \geq 36,000 \text{ assuming complete conversion to the triplet.}$$

This gives us a fairly close bracketing of the extinction coefficient. One final point is worth mentioning. Because, with this new technique, the excitation region is extended to shorter wavelengths, where the singlet absorption is much higher, experiments can be conducted with solutions of much lower concentration. Singlet depletions will therefore be larger and the lower limits for ϵ_T , obtained by assuming complete conversion, will approach much closer to the true value.

Generalization of Lambert's Absorption Law

Using the above technique, it has been found that the mercury lamp, used as a source for the absorption measurements, itself produces a significant conversion of molecules to the triplet state. The reason for this is that, although the intensity of the lamp is many orders of magnitude less than the flash used for excitation, it is shining on the sample for a very much longer period of time. It was not immediately obvious whether or not this would complicate or even invalidate the measurements. Under these conditions the singlet depletion caused by the source light will be a function of distance through the specimen, as well as of wavelength. The analysis given in Appendix A was, therefore, carried out. The final equation obtained (Appendix, Equation 24) is,

$$\epsilon_T = \frac{\log I_T'/I_T''}{\log I_S'/I_S''} \epsilon_S$$

where I_T' and I_S' are the transmitted intensities in the presence of triplet-singlet conversion caused by the measuring light source, (as measured by the deflections of the oscilloscope trace from its level for zero intensity), and I_T'' and I_S'' are the corresponding deflections in the presence of the further conversion caused by the flash. The subscripts T and S refer to the triplet and singlet wavelengths, respectively.

It is necessary, therefore, to measure only four experimental quantities, I_T' , I_T'' , I_S' and I_S'' and to know ϵ_S , whose value can be measured independently on a normal double-beam spectrophotometer or taken from the literature. All the above measurements can be obtained with a single specimen. No blank specimen is needed, since the zero level of the oscilloscope trace (no light transmitted) is readily obtained.

IV. Quantum Yields of Triplet Formation

(Supported by STL Independent Research Program)

The quantum yield of triplet formation is an important parameter in evaluating triplet states as agents for flash blindness protection. Although this is a difficult parameter to measure directly, an upper limit may be estimated as the difference between unity and the quantum yield of fluorescence ϕ_F , since excited molecules which do not fluoresce do not pass into the triplet state. Similarly the quantum yield of phosphorescence emission from the triplet state would be a lower limit. Thus, the quantum yields may be bracketed between these upper and lower limits.

A schematic diagram of the quantum yield apparatus used is given in Figure 9. The apparatus was checked by measuring fluorescence yields of several standard compounds, and results agree well with literature values, as shown in Table II. Apparatus was modified to make possible measurements in the range between liquid nitrogen and room temperature. A galvanometer type of temperature controller monitored injection of coolant into a dewar arrangement to maintain the desired temperature. Because of difficulty in the measurement of optical density at low temperature, a further modification was carried out so that the optical densities could be determined within the instrument through direct measurement of light transmission.

Quantum yields of fluorescence ϕ_F , as well as $1-\phi_F$, for several aromatic molecules in deoxygenated solvents are listed in Table II, together with available literature values. Perylene is the only one of these compounds which may be eliminated from consideration as a photochromic material on the basis of fluorescent yield measurements. Its fluorescence yield of approximately 100% implies a very poor conversion to the triplet state. All of the other compounds have values of ϕ_F between 30% and 10%. Corresponding yields of triplet could therefore be as high as 70% to 90%, assuming no

Table II

Quantum Yields of Fluorescence and Triplet Formation

Molecule	Solvent	Quantum Yield of Fluorescence (STL Value)	$1-\phi_F$	ϕ_F (Literature Values)		
				(a)	(b)	(c)
Naphthalene	ethanol	.26	.74			
	n-hexane	.20	.80			
Anthracene	benzene	.27	.73	.256	.29	
	ethanol	.23	.72	.270	.30	
	n-hexane	.29	.71	.316	.31	
Phenanthrene	benzene	.14	.36			
	ethanol	.125	.875		.10	.2
Perylene	benzene	1.00	.00	.89		
	ethanol	1.01	ca .00	.87		
	n-hexane	.93	.02	.88		.98
Naphthochrysene	benzene	.21	.79			
	ethanol	.18	.82			
Naphthocoronene	benzene	.255	.745			
Chrysene	ethanol	.17	.83			
Coronene	benzene	.23	.77			.3
	ethanol	.20	.80			(in chloroform)
Triphenylene	ethanol	.10	.90			
Picene	ethanol	.26	.74			
	benzene	.23	.72			
1,2,3,4 Dibenzo- anthracene	benzene	.20	.80			
	ethanol	.20	.80			

(a) Weber, G., and F. W. J. Teale, Trans. Faraday Inc. 53, 646 (1957).

(b) Melhuish, W. H., J. Phys. Chem., 65, 299 (1961).

(c) Bowen, E. J., Advances in Photochemistry, Vol I, p. 32, Interscience Publishers (1963).

radiationless deactivation of the fluorescent state to the ground state is present.

Because of the large energy gap between the fluorescent state, S_1 , and the ground state, S_0 , (greater than $25,000\text{cm}^{-1}$ for most compounds), its short radiative lifetime ($\sim 10^{-8}\text{sec}$) and the absence of any electronic states, except triplet states, in between, the above assumption is probably quite a good one. Confirmation could be obtained by measuring the phosphorescence yields of several fully deuterated compounds such as perdeuteronaphthalene, C_{10}D_8 , and perdeuteroanthracene, $\text{C}_{14}\text{D}_{10}$. In the perdeuterated compounds, non-radiative deactivation of the triplet state, T_1 , is probably reduced effectively to zero, so that the triplet yield, ϕ_T , and the phosphorescence yield, ϕ_P , should be identical (8). In ordinary perprotonated compounds radiationless deactivation of T_1 is always present, so that ϕ_P gives only a lower limit to the value of ϕ_T .

All the measurements in Table II were made with fluid solutions. However, the observed low sensitivity of ϕ_F to change of solvent and the short lifetime (10^{-8}sec) of S_1 makes it highly probable that ϕ_F will be substantially unchanged in a plastic medium.

In conclusion we see from Table II that triplet yields, as measured by $(1-\phi_F)$ appear to be gratifyingly high. Thus triplet states appear especially favorable for application in automatic light filters for protection against flash blindness.

V. Studies of Triplet States in Plastics

A. Triplet State Lifetimes

Triplet lifetimes of several compounds, dissolved in cross-linked polymethylmethacrylate (PMM), have been measured by observing the rate of decay of triplet-triplet absorption with a photomultiplier, following excitation by a single flash. The values obtained at 24°C are listed in Table III. In general, these values are about a factor of 2 smaller than lifetimes measured in frozen glasses at liquid nitrogen temperatures. This implies that some non-radiative contribution to the decay rate still occurs in our plastic media at room temperature. It may be possible to reduce this non-radiative contribution by using a different matrix, or by the use of perdeuterated compounds as discussed in Section IV. However, we see that the measured lifetimes lie in the desired range (a few seconds) for a flash-blindness device.

Table III

Phosphorescent Lifetimes of Aromatic Compounds
in Cross-Linked PMM at 24°C

Compound	τ (sec.)	Estimated Accuracy %
Anthracene	0.070	± 10
Chrysene	1.2	± 10
Coronene	3.4	± 40
Naphthocoronene	0.52	± 20
Phenanthrene	1.4	± 10
Picene	1.3	± 10

B. Fatigue Studies

At high light intensities, photochemical reactions which are not significant under low level irradiation may assume importance. The reason is that, at high intensities, high concentrations of intermediates, such as the triplet itself, are present. Thus it is important to observe the behavior of plastics during repetitive exposure to high-intensity flashes of light.

A preliminary study was made of a PMM rod containing chrysene at 10^{-4} molar concentration. When subjected to 50 flashes, each of 450 joules, spaced at 5 min. intervals to avoid excessive heating, no observable difference could be detected between the spectra before and after the test. A later test of 700 flashes on the same material produced no damage except minor crazing of the surface due to heating of the plastic. No changes in the absorption spectrum could be detected after flashing, showing that the triplet compound itself was unaffected. Thus it does not appear that fatigue at flash intensities is likely to be a problem. However, fatigue tests should be extended to additional compounds.

C. Improved Plastic Media

Three different families of epoxy polymers, having respectively aromatic, aliphatic, and alicyclic structures, have been investigated. These provide a spread of molecular weights, degrees of cross-linking and variations of molecular environment. The objective was to obtain a plastic with a more rigid internal structure. The epoxies as found on the industrial market are primarily used and intended for potting and encapsulation applications - and these are not cured with catalyst and copolymer ratios which yield good optical samples. For this reason, it has been necessary to pick out of the wide field of epoxies, those monomers which can be had with minimum starting color, and for which there is the possibility of working out catalyst-copolymer ratios which yield a final product of tolerable color level.

Most epoxies obtainable previously were unsatisfactory because of strong absorption in the visible spectrum. One of the recently studied aromatic epoxies, however, has only a slight visible color and is only a little less transparent in the ultraviolet than PMM. In addition, the solubilities of aromatic compounds in this epoxy are an order of magnitude higher than in PMM. Samples containing chrysene at a concentration of 10^{-2} Molar have been made and concentrations up to 10^{-1} M appear possible.

The higher solubilities possible using epoxies permits us to reduce the thickness of a plastic sample and still have it show a good development of T-T absorption under irradiation. Using a special Teflon mould, we have successfully cast several goggle lenses from both PMM and the new epoxy, using chrysene as the solute. Whereas the PMM lenses show little color development under sunlamp irradiation unless they are first cooled in liquid nitrogen, the epoxy lenses develop a good coloration even at room temperature. Apparently the epoxy matrix is more efficient at inhibiting non-radiative deactivation of the triplet. These goggle lenses represent the closest approach so far to a prototype device, being approximately two inches square and between 2 and 3 mm thick.

D. Microscopic Structure of the Plastic Medium

(Supported by STL's Independent Research Program)

It is of fundamental interest to know how the microscopic structure (e.g. crosslinked or not) of the plastic medium affects such parameters as the lifetime of the triplet state and the rate of diffusion of atmospheric oxygen into the plastic (which may play a role in photochemical fatigue). Preliminary studies in this area have therefore been made. This phase of the program has been supported by STL's Independent Research Program and was summarized in the last semi-annual report (2). Experiments to measure the retardation spectrum of various plastic samples have been designed with the objective of distinguishing between truly cross-linked

specimens and those in which the polymer chains are extensively tangled but not actually cross-linked chemically. Measurements of the elastic moduli of the specimen as a function of temperature and the rate and extent of deformation with time under a constant load are required. The physical reasoning behind the method is as follows: under a constant stress a difference between cross-linked and highly-tangled polymers should begin to show up after a long period of time. For a tangled polymer, deformation should continue almost indefinitely, since the tangling forces will be of a Van der Waal's character and tangles should progressively break under a constant load. For a truly cross-linked plastic, on the other hand, cross-links which are chemical in nature are present in addition to tangles. Consequently, a plateau should eventually be reached, beyond which further deformation would require the breaking of chemical bonds. This would not take place without a large increase in load.

Calculations show that for our plastics, experiments need to be carried out between 100 and 125°C. A thermostatted chamber, designed for stress relaxation measurements, is available at STL but several modifications are needed to allow its use in the above temperature range. This work does not command a high priority, but if such modifications prove feasible, the above measurements will be attempted and the results will be given in a later report.

E. Polymerization Under Pressure

During the past year techniques for carrying out polymerization of various plastics under pressure have been perfected. A photograph of the autoclave used, together with a selection of large diameter plastic samples is given in Figure 10. A detailed description of the techniques and the temperature-time curing cycles used, was given in the last semi-annual report (2). The main advantages of polymerizing under pressure are the reduced curing times (24 hrs. instead of up to 3 weeks) and the suppression of void and bubble formation in the specimen.



Figure 10. Autoclave for Polymerization under Pressure
and Large Diameter Plastic Specimens

VI. Evaluation of Materials for Flash Blindness Protection

A. Passive Systems

The most desirable type of automatic light filter for flash blindness protection would be one that has high enough sensitivity to attain the required optical density in response to the uncoming radiation alone. Such a device can be termed a passive system, in contrast to one in which the incoming light triggers an auxiliary light source which then operates the light filter.

An analysis of the requirements of a passive device has been given in previous reports under this contract (1,3) and is summarized in Section I of the present report. Metcalf and Horn (1) found that the maximum exposure, for which the recovery time (to see a test stimulus of 7Ft. lamberts luminance) was immediate, was 3200 lumens/cm² for a 0.1 sec exposure. This exposure is equivalent to 1.33×10^{-4} cal/cm² of visible energy. To keep the actual exposure below this figure, for a fireball with an effective black-body temperature of 7600°K, a triplet state compound must satisfy the condition,

$$\epsilon \theta \geq 2.3 \times 10^5$$

where ϵ is the molar decadic extinction coefficient for the T-T absorption and θ the quantum yield of conversion to the triplet state. In obtaining the above relation, it is assumed that only radiation between 3200 and 6900Å is effective in operating the filter.

Naphthocoronene, the most promising compound studied to date, has a peak ϵ greater than 10^5 and a θ of 0.8. A combination of coronene, naphthocoronene and naphthocrysene could provide a filter with an ϵ of 10^5 or more over most of the visible spectrum still maintaining θ at about 0.8. Such a filter comes within a factor of three of satisfying the above condition. As to the

possibility of further improvements, the upper limit for θ is 1.0, and for ϵ the highest figures observed for some natural pigments such as chlorophyll are about 5×10^5 . The theoretical limit to ϵ is probably about 10^6 . The area of most uncertainty is the value of ϵ and this is why we have devoted much effort during the past year to attempts to reduce the uncertainties in the measurements. To summarize, it does not seem out of the question to find a combination of triplet state compounds which would satisfy the above condition and thus give protection against flash blindness in a passive system. What we most need to complete the evaluation are more reliable measurements of T-T extinction coefficients.

However, there is some reason to believe that, in actual field conditions, flash blindness could occur at incident light levels somewhat lower than those obtained in the experiments of Metcal and Horn. This might especially be so in the case where an individual happens to be looking exactly in the direction of the fireball, and therefore forms a focussed image of the fireball on the fovea. In addition, there is also the possibility of a situation where a large part of the U-V component of the incident radiation is removed by scattering before it reaches the eye. Under these conditions a still higher value of $\epsilon \theta$ is needed to give protection. Since the theoretical upper limit is probably about 10^6 , using $\epsilon = 10^6$ and $\theta = 1$, it is wise to consider the possibilities of using a non-passive system. This is discussed below.

B. Activated Systems

An activated system is one in which an auxiliary flash lamp light source, close to or actually built into the protective device, is used to operate the photochromic filter. This device

must be triggered, with the minimum delay, by the first rays of light received from the nuclear weapon. Use of an auxiliary source of excitation makes it possible to relax the condition,

$$\epsilon \phi \geq 2.3 \times 10^5$$

required for a system which must depend on the incident radiation alone. Also, by the use of suitable static filters, the excitation can be confined to the most effective region of the ultra-violet required to excite the particular compound employed in the photochromic filter. However, it is still desirable to reduce the required excitation level to a minimum, in order to keep down the weight of the power supply and storage capacitors needed to operate the flash lamp. A system with the highest possible value of $\epsilon \phi$ is, therefore, still desirable. Thus the overall objectives of the present program, viz. to find compounds with broad T-T absorption, values of ϵ exceeding 10^5 , and with ϕ as close as possible to 100%, are unchanged for an activated system.

Given the values of ϵ , ϕ and T-T absorption bandwidth, the relative sensitivity of each compound as a photochromic light filter can be calculated. The U-V energy (3200-4000Å) which must be absorbed to produce T-T absorption of optical density 1 in the visible is (This Report, Section I, Equation 1),

$$E = \frac{78}{\epsilon \phi} \text{ cal/cm}^2$$

To reach optical density 4, the corresponding relation is,

$$E = \frac{312}{\epsilon \phi} \text{ cal/cm}^2$$

Using this expression, the required U-V energy exposures for several values of $\epsilon \phi$ have been calculated and are summarized in Table IV below.

Table IV

Amount of U-V Energy Required for OD = 4 as Function of
Value of $\epsilon \bar{\nu}$

$\epsilon \bar{\nu}$	E_4 cal/cm ² (3200 - 4000Å)
10^6	3.12×10^{-4}
10^5	3.12×10^{-3}
10^4	3.12×10^{-2}
10^3	3.12×10^{-1}

The best compound found to date, naphthocoronene, has $\epsilon \bar{\nu} \sim 3 \times 10^4$, taking 4×10^4 as the average value of ϵ across the visible region. This gives $E_4 = 10^{-2}$ cal/cm². It should be possible to provide this level of U-V excitation over an area of about 100cm² with a single electronic flash of about 1000 joules total energy. The weight of power supply and storage capacitors for this energy is of the order of 100 lbs, but could probably be reduced if repetitive flashing at frequent intervals was not necessary. The duration of such a flash could easily be made less than 10^{-4} sec and could probably be reduced to about 2×10^{-5} sec. Such a system ought to provide adequate protection against the flash of a nuclear weapon. It is recommended that plastic samples be evaluated under known levels of U-V irradiation in future. The output of the flash source should be measured by uranyl oxalate or potassium ferrioxalate actinometry (9).

C. Methods of Excitation Other than Light

In principle, conversion to the triplet state can be brought about by other forms of excitation, as for example, by X-rays, γ -rays or by electrons. No information is available for X-ray or γ -ray excitation but studies of triplets produced by electron irradiation have been reported by McCollum and Wilson(10). These authors studied the production of triplet states in naphthalene, anthracene and phenanthrene by pulsed electron irradiation. G (triplet)^{for}/anthracene was found to be 0.5 for a dose of 10^{18} eV/g. The largest value accountable for by mass absorption by the solute alone is 0.02. It appears, therefore, that energy transfer from solvent to solute is taking place. A dose of 10^{18} eV/g corresponds to about 2.4×10^{-2} cal/g. For a 2×10^{-3} M solution of anthracene in paraffin oil, this dose produced a concentration of 7.2×10^{-6} M of triplet in a cell 2.5cm long by 2.2cm diameter. For a cell of this size, the dose rate of 2.4×10^{-2} cal/g is equivalent to about 4×10^{-2} cal/cm². Since, for anthracene, the triplet extinction is $\epsilon = 71,500$, this dose produces an optical density of about 1.3 for the 2.5cm path length. Using $\phi = 0.7$, we find from Table IV that, for U-V excitation, an OD of 4 can be achieved with 6×10^{-3} cal/cm². For an OD of 1.3 the figure is 2×10^{-3} cal/cm². Thus excitation by U-V is about twenty times more efficient than by electron irradiation.

This result is, perhaps, not surprising since excitation by 8 MeV electrons is bound to be more wasteful of energy than excitation by ultra-violet light. Electron irradiation first produces highly excited upper states and ionized species. These then tumble down to lower levels and eventually over to the lowest triplet state. However, a large fraction of the absorbed energy is converted into heat in the process. We conclude that, for a device to provide protection against flash blindness, excitation by U-V light is much to be preferred over electron

irradiation. In addition, the use of electron excitation would probably incur a much heavier weight penalty for the electron accelerator plus the shielding necessary to protect personnel.

D. Conclusions and Recommendations for Future Work

To sum up it appears that the triplet states of aromatic compounds warrant continued investigation as automatic light filters for protection against flash blindness. The probable necessity that the eventual device will be activated by an auxiliary flash source, should be borne in mind and the data obtained should be evaluated in this context. Other methods of excitation, such as electron irradiation, do not appear to be competitive with excitation by U-V light. Accordingly the following program of work is recommended for next year.

1. Improved measurements of T-T extinction coefficients and quantum yields of fluorescence and phosphorescence.
2. Chemical synthesis of larger quantities (e.g. 5 gms) of the more promising triplet state compounds, such as naphthorone, and their derivatives, to facilitate further evaluation in plastic media.
3. Preparation and study of the properties of plastics containing combinations of two or more triplet state compounds, with the object of making a neutral filter for the visible region of the spectrum.
4. Development of techniques for fabricating photochromic plastic specimens in sheets up to 1 inch thick and 1 ft² in area.
5. Construction of apparatus for measuring the amount of U-V excitation necessary to produce a given optical density of T-T absorption for various samples.

APPENDIX A

Lambert's Absorption Law for a System in
which the Measuring Beam Causes Singlet Depletion

In its usual form Lambert's absorption law expresses the transmitted intensity as

$$I_{\lambda} = I_{0\lambda} e^{-\alpha_{\lambda} \ell} \quad (1)$$

where $I_{0\lambda}$ is the source intensity at wavelength λ impinging on the specimen, α_{λ} is the absorption coefficient, and ℓ the path length through the absorber. In the case to be considered here, α_{λ} is also a function of distance x , so that we must write

$$I_{\lambda} = I_{0\lambda} \exp \left[- \int_0^{\ell} \alpha_{\lambda}(x) dx \right] \quad (2)$$

Generally, α_{λ} can be written as a product

$$\alpha_{\lambda}(x) = k_{\lambda} c(x) \quad (3)$$

where k_{λ} is not a function of x and is the absorption coefficient per unit concentration, and $c(x)$ is the concentration (per unit length and cross section) of absorber. With this substitution Lambert's law is called Beer's law. Substituting (3) in (2) gives

$$I_{\lambda} = I_{0\lambda} \exp \left[-k_{\lambda} \int_0^{\ell} c(x) dx \right] \quad (4)$$

Now let us consider the form of $c(x)$ and determine whether this will make a difference in the way k_{λ} is to be measured.

For the new concentration of absorber in the ground state (singlet) we can write

$$c_s^i(x) = c_s - c_T^i(x), \quad (5)$$

where c_s is the original concentration without any depletion caused by the source lamp, and $c_T^i(x)$ is that part removed by

absorption of energy from the source under the assumption that all of $c_T^i(x)$ goes to produce a concentration of triplet. Now

$$c_T^i(x) = -n k_\lambda c_S x I_\lambda(x), \quad (10)$$

where the proportionality constant n is related to the quantum efficiency of conversion from singlet to triplet and has the units of concentration included.

Substituting $I_\lambda = I_{0\lambda} e^{-k_\lambda c_S \ell}$ in (10), (10) in (5), then (5) in (4), we have

$$I_\lambda = I_{0\lambda} \exp \left[-k_\lambda \int_0^\ell (c_S + n k_\lambda c_S x I_{0\lambda} e^{-k_\lambda c_S x}) dx \right] \quad (11)$$

Evaluating the integral gives

$$c_S \ell - \frac{n I_{0\lambda}}{k_\lambda c_S} \left[(1 + k_\lambda c_S \ell) e^{-k_\lambda c_S \ell} - 1 \right] \quad (12)$$

which reduces to the usual form when $n = 0$.

Because the two concentration factors are separable, we can separate the effects of depletion from different sources. If the singlet is depleted still further by application of the photolysis flash, we have

$$c_S''(x) = c_S^i(x) - c_T''(x,r) = c_S - c_T^i(x) - c_T''(x,r), \quad (13)$$

where $c_T''(x,r)$ is the additional concentration depletion but is of sufficiently complex form that we shall not attempt to derive it here. The form of (13), however, shows that the concentration factors are still separable, so that one may write finally

$$I_\lambda = I_{0\lambda} \exp(-k_\lambda c_S \ell) \exp(k_\lambda c_T^i \ell) \exp(k_\lambda c_T'' \ell), \quad (14)$$

where c_T' and c_T'' are now written as concentration per unit length times length, as was c_S .

To go further and consider actual measurements using Equ. such as (14), let us write Beer's law in terms of optical densities using logs to the base 10 instead of e , giving ϵ_λ as the extinction coefficient per unit concentration, where $\epsilon_\lambda = \frac{\kappa_\lambda}{\ln_e 10}$. Using subscripts s for singlet and T for triplet, we can write

$$D_s = \log \frac{I_o}{I_s} = \epsilon_s c_s \ell \quad (15)$$

for singlet with no depletion,

$$D_s' = \log \frac{I_o}{I_s'} = \epsilon_s c_s' \ell \quad (16)$$

for singlet with depletion caused by the light source, and

$$D_s'' = \log \frac{I_o}{I_s''} = \epsilon_s c_s'' \ell \quad (17)$$

for further depletion caused by the flash.

Here $c_s' = c_s - c_T'$, and $c_s'' = c_s - c_T' - c_T''$. Then

$$D_T = 0 \text{ when } c_T = 0, \text{ and} \quad (18)$$

$$D_T' = \log \frac{I_o}{I_T'} = \epsilon_T c_T' \ell \quad (19)$$

analogous to (16), and

$$D_T'' = \log \frac{I_o}{I_T''} = \epsilon_T (c_T' + c_T'') \ell \quad (20)$$

analogous to (17).

Subtracting (19) from (20)

$$D_T'' - D_T' = \epsilon_T c_T'' \ell. \quad (21)$$

Subtracting (17) from (16)

$$D_S' - D_S'' = \epsilon_S (c_S' - c_S'') \ell = \epsilon_S c_T'' \ell. \quad (22)$$

Solving (21) for ϵ_T

$$\epsilon_T = \frac{D_T'' - D_T'}{c_T'' \ell}$$

and (22) for $c_T'' \ell = \frac{D_S' - D_S''}{\epsilon_S}$ and substituting the latter in the former, gives

$$\epsilon_T = \frac{D_T'' - D_T'}{D_S' - D_S''} \epsilon_S \quad (23)$$

It should be noted that, since Eq. (23) involves a difference of densities for singlet and triplet, the measurement of I_0 (equivalent to $I_0 - 0$) is not necessary in this case, for

$D_S' - D_S''$ may be written:

$$\log \frac{I_0'}{I_S'} - \log \frac{I_0''}{I_S''} = \log \frac{I_0'/I_S'}{I_0''/I_S''} = \log \frac{I_S''}{I_S'}, \text{ and}$$

similarly for $D_T'' - D_T'$. Hence Eq. (23) may also be written

$$\epsilon_T = \frac{\log I_T'/I_T''}{\log I_S''/I_S'} \epsilon_S \quad (24)$$

Thus the blank specimen need not be used, so long as the zero level (no light transmitted) is known. Therefore, Eq. (23) may be applied after measurement of four experimental quantities, i.e., I_T' , I_T'' , I_S' , and I_S'' , along with the assumption that ϵ_S is known for the wavelengths of interest. However, ϵ_S may be measured more conveniently and accurately by a double-beam method.

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